CHAPTER 2

LITERATURE REVIEW

2.1 Properties of Si_3N_4 ceramics

There are many kinds of engineering ceramics, such as silicon nitride, silicon carbide, alumina and zirconia. In particular, silicon nitride (Si_3N_4) has been the most attractive material for structural engineering applications. Si_3N_4 has been widely used because of its properties, including high strength over a wide range of the temperature, good thermal shock resistance, strong wear resistance, and corrosive resistance.23)

Table 2.1 shows the physical and chemical properties of Si_3N_4 ceramic compared with other ceramics that are candidates for structural engineering applications.23) This Table suggests the properties of Si_3N_4 is superior to the other materials. Si_3N_4 has low density, high fracture toughness, and also high fracture strength. Moreover, Si_3N_4 has better thermal shock resistance than other materials because of the lowest thermal expansion (CTE), and high strength. Therefore, Si_3N_4 is the material that suitable for use in engineering applications such as engine components, wear-resistant parts, bearing balls, and cutting tools.

Table 2.2 and Fig. 2.1 show typical Si_3N_4 components, for several application fields. Some heat or wear resistant components such as mechanical seals, cutting tools and glow plugs are shown.24)

Table 2.1 Physical and mechanical properties of ceramics that are candidates for structural engineering applications.[23)]

Material	$T_{melting}$ (^oC)	Thermal expansion, CTE ($10^{-6}\ {}^oC^{-1}$) to ~ 1000 ^oC	Young's Modulus @ 21 ^oC (GPa)	Density (g/cm^3)	Fracture toughness @ 21 ^oC ($MPa\ m^{1/2}$)	Flexural Strength @ 21 ^oC (MPa)	Flexural strength @ 1200 ^oC (MPa)
SiC^1	2250#	2.8	342	3.02-3.16	2.6-3	-	
SiC^2	2400#	4.3	420	3.10	3.5	530	-
SiC^3	2400	4.8	390-480	3.08-3.20	2.5-5.6	400-870	276-690
$Si_3N_4{}^1$	1900*	1.4	274	3.02-3.26	4.0-5.5	376	275
$Si_3N_4{}^2$	1900	2.3-3.0	100-200	2.1-2.6	3-4	150-295	160-300
$Si_3N_4{}^3$	1900	3.0-3.5	240-330	2.9-3.5	4-7	400-1000	350-1000
$Si_3N_4{}^4$	-	-	-	-	6.5-7.5	700-950	550-830
Al_2O_3	2045	9.0	360	3.61-3.97	2.5-4.0	300-450	150
$Al_2O_3{}^5$	-	-	-	-	7.5-9.5	650-800	-
ZrO_2	2700	10.0	200	5.73-6.07	4.4	-	-
$ZrO_2{}^6$	-	-	-	-	2.3	100-300	-
$ZrO_2{}^7$	2715	8.7-11.4	150-260	5.6-6.1	15-18	700-1200	< 500
$ZrO_2{}^8$	-	-	-	-	5-16	> 1000	-

\# Decomposition temperature in vacuum

* Decomposition temperature in 10^5 Pa of N_2 gas

[1] Hot pressed ceramics

[2] Reaction sintered ceramics

[3] Sintered ceramics

[4] Composite Si_3N_4 with 30 vol% SiC whiskers

[5] Composite Al_2O_3 with 20 vol% SiC whiskers

[6] Fully stabilized ZrO_2

[7] Partially stabilized ZrO_2

[8] Tetragonal zirconia polycrystalline, TZP

Table 2.2 Expected fields of application of Si_3N_4 ceramics.[24)]

Application fields	Components
Engine components:	
Diesel	Plugs, turbocharger rotors
Wear and corrosion resistant components	Bearings, mechanical seals, blast honing nozzles, vane pump parts, chemical pump parts, milling balls
Metal treatment components	Aluminum diecast parts (metal melt guides, plungers, cylinders, and piston cylinders); wire-drawing roller pulleys and dies; steel forming parts
Tools	Cutting tools
Heat resistant jigs:	
Heat protecting parts	Thermal insulation ceramic tiles, heat shielding plats, plasma insulators
High temperature test jigs	Strength test jigs (bend and tensile)

Fig 2.1 Silicon nitride components, including other materials (Partially stabilized zirconia (white) and alumium substrates (thin plates)).[24)]

2.2 Basic knowledge about crystal structures of Si_3N_4

The puckered sheet of Si_3N_4 crystal structure, which joins Si-N ring, is shown in Fig 2.2.[25)]

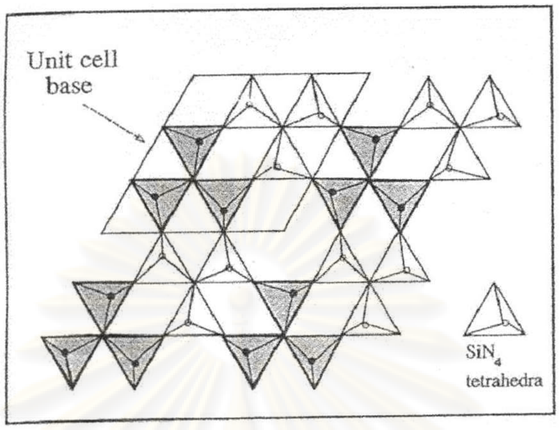

Fig 2.2 Outline of silicon nitride crystal structure

The tetrahedra structure (SiN_4) is the basis of crystalline Si_3N_4.[25)] Silicon atom is coordinated by four nitrogen atoms as shown in Fig 2.3a.[26)] It is indicated that the SiN_4 tetrahedra introduces an open structure with large voids. Moreover, two crystalline forms of Si_3N_4, which is α and β phases, are shown by X-ray diffraction (XRD) pattern. Although both phases are hexagonal structure, the sequence of Si-N layers is arranged differently in c-axis direction.

Fig 2.3-b shows the A-B-A-B stacking sequence of β-Si_3N_4. The next A-B layer is directly over the first. Therefore, a continuous interstitial channel parallel to the c-axis forms around the site surrounded by 12 Si-N bonds. α-Si_3N_4 has an A-B-C-D stacking sequence of Si-N layers. Fig 2.3-c shows the A-B-C-D stacking sequence of α-Si_3N_4. The C-D layer is filled on the A-B layer and creates isolated large interstices formed by the 12-member rings. Furthermore, the layers of α-Si_3N_4 stacking repeat after twice the number of A-B layer of β-Si_3N_4. Consequently, the microstructure of α-Si_3N_4 is equiaxed grains and has approximately twice the c-axis of β-Si_3N_4. In the other words, the microstructure of β-Si_3N_4 is columnar grains and has a half c-axis of α-Si_3N_4.

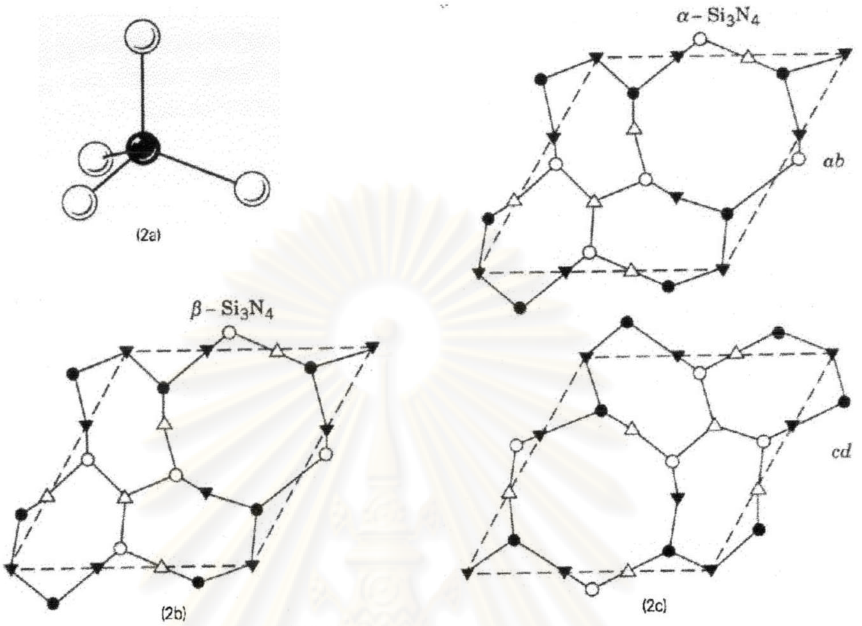

Fig 2.3 (a) The basis of crystalline Si_3N_4 tetrahedra. (b) A-B layer, which is repeated in the A-B-A-B stacking sequence of β-Si_3N_4. (c) A-B and C-D layer, which are alternated in the stacking sequence of α-Si_3N_4.[26)]

2.3 Sintering mechanism of Si_3N_4 ceramics

Si_3N_4 has been currently used since it has superior properties such as mechanical strength, high fracture toughness and chemical stability at room and high temperatures. However, pure Si_3N_4 is difficult to densify because of the high covalent nature (Approximately 75%) of the Si-N bonds.[1-3)] In general, oxide additives promote densification by liquid phase sintering mechanism. Metal oxide additives such as CeO_2, La_2O_3, Sm_2O_3, Y_2O_3, Al_2O_3 and MgO are used as sintering additives. The Y_2O_3 and Al_2O_3 system is the most popular oxide additives for Si_3N_4 ceramics.[5, 10)]

In common, dense β-Si_3N_4 bodies are sintered from α-rich starting powder containing 3-7 vol. % β-Si_3N_4.[10, 14)] Besides, these sintering additives react with surface

SiO_2 of the Si_3N_4 powder and form a grain boundary glassy phase. These phenomena assist rearrangement of particle to achieve the densification.[27)]

The solution precipitation mechanisms during liquid phase sintering are shown in Fig 2.4: α-Si_3N_4 solute to glass phase, and $\alpha \rightarrow \beta$-Si_3N_4 phase transformation followed by the rod like β-Si_3N_4 grain growth occur.[28-29)]

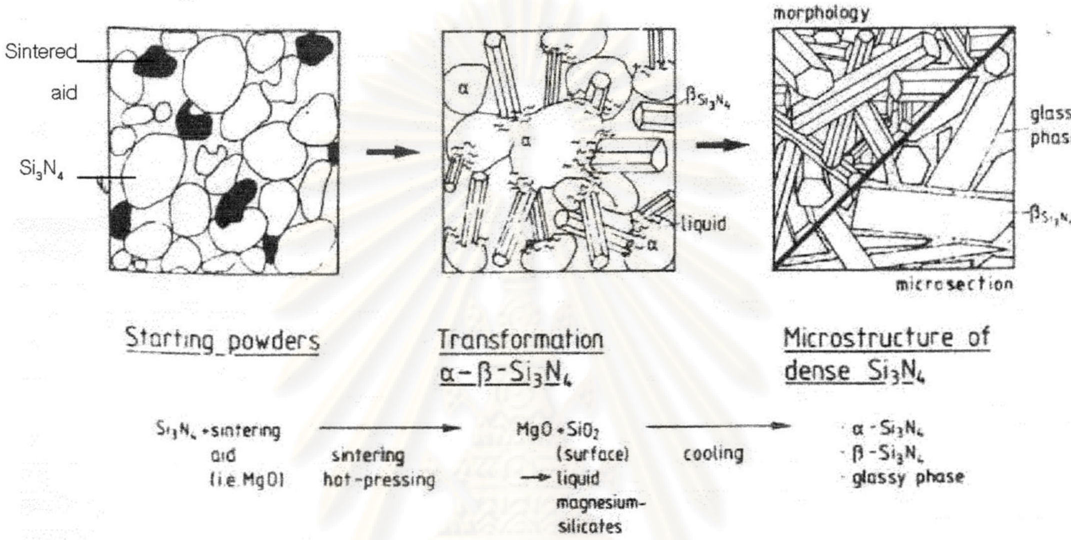

Fig 2.4 Schematic representation of the solution precipitation mechanism during liquid phase assisted densification of Si_3N_4.

The behaviors of nucleation and phase transformation are affected by the mass transport through the glassy phase during the liquid phase sintering. With increasing temperature, the liquid phase composition changes to an oxynitride by preferred dissolution of α-Si_3N_4 particle and leads to re-precipitation of β-Si_3N_4. The high viscosity of oxynitride melt reduces the β-nucleation rate, provided the high aspect ratio, which improves the mechanical properties.[28)]

2.4 Instability of Si_3N_4 and Si_3N_4 ceramics

Si_3N_4 is thermodynamically unstable with respect to oxidation. Moreover, Si_3N_4 decomposes at high temperature and Si_3N_4 ceramics show mass loss reaction during sintering.

2.4.1 Oxidation of Si_3N_4

The oxidation occurs by two mechanisms, passive oxidation and active oxidation as shown in reaction (1) and (2).[21)]

$$Si_3N_4\,(s) + 3O_2\,(g) \rightarrow 3SiO_2\,(l) + 2N_2\,(g) \qquad \text{---------}(1)$$

$$2Si_3N_4\,(s) + 3O_2\,(g) \rightarrow 6SiO\,(g) + 4N_2\,(g) \qquad \text{---------}(2)$$

Under low oxygen pressure ($\sim10^{-2}$ bar (10^{3} Pa) at 1000 ^{O}C), active oxidation occurs with formation of volatile SiO. A SiO_2 protective layer is formed on a surface of specimen by passive oxidation in the P_{O2} region of $\geq 10^{2}$ Pa.

2.4.2 Decomposition of Si_3N_4

Silicon nitride does not have a melting point but decomposes under 0.1 MPa N_2 at 2173 K. From the thermodynamic viewpoint, Si_3N_4 (s) decomposes to Si (g) and N_2 (g) at the sintering temperature in vacuum according to following reaction:[31)]

$$Si_3N_4\,(S) \rightarrow 3Si\,(l) + 2N_2\,(g) \qquad \text{---------}(3)$$

From the stability diagram for Si_3N_4, nitrogen gas pressure as high as $P_{N2} > 10^{6}$ Pa is essential to obtain dense Si_3N_4 ceramics at high sintering temperature. In the other words, high N_2 gas pressure in the furnace effectively suppresses the mass loss during sintering.

2.4.3 Mass loss of Si_3N_4 ceramics during sintering

Yokoyama et al., studied the stability of Y_2O_3-Al_2O_3-SiO_2 glass composition at 2023 K under 0.1 MPa of N_2 to examine its thermodynamic stability at sintering temperature.[18-21)] The results indicated that Y_2O_3 and Al_2O_3 are more stable than SiO_2 in Si-Y-Al oxynitride glass. Thus, the mass loss of the glass during heat treatment comes from the vaporization of SiO as shown in reaction (4). The N_2 gas pressure in the atmosphere does not affect the reaction.

$$Si_3N_4\,(s) + 3SiO_2\,(l) \rightarrow 6SiO\,(g) + 2N_2\,(g) \qquad \text{----------(4)}$$

When reaction (4) occurs, oxygen contents in the specimen decreases. Furthermore, the amount of vaporized SiO (g) and N_2 (g) is same with mass loss. Thus, it is important to minimize mass loss because it leaded to composition change and mechanical property degradation.

2.4.4 Sintering of Si_3N_4 ceramic in air furnace

Non-pressurized sintering of Si_3N_4 ceramic in N_2 gas furnace is thought to be a low cost fabrication. But N_2 gas furnace is still special comparing to air furnace. According to Wada et al. in 2001, Si_3N_4 ceramic could be sintered without serious oxidation in air atmosphere furnace.[22)] To isolate Si_3N_4 specimen from air. Si_3N_4 specimen is set in two Al_2O_3 crucibles that are filled with Si_3N_4 powder in the inner crucible and Al_2O_3 powder in the outer crucible. Using packing powder, most of oxygen in crucible reacts with the Si_3N_4 powder, because it has large surface area, before reacts with specimen. In other words, Si_3N_4 powder generates gasses through equation (4) and is active oxidation. By oxidizing the Si_3N_4 packing powder intentionally, much gas generates. The generated gases disturb air diffusion into the crucible. Thus, Si_3N_4 specimens do not react with oxygen. Therefore, Si_3N_4 ceramics could be sintered without serious oxidation and mass loss in air atmosphere furnace.